

Acetylation of Alkyl Lactates and Similar Hydroxy Esters with Acetic Acid

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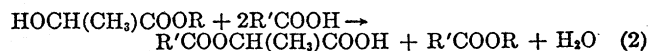
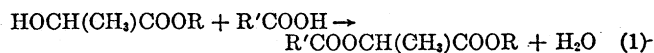
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Alkyl lactates have been acylated conveniently and in high yields with acid anhydrides, acid chlorides, and ketene, but prior to the present investigation little was known about the suitability of organic acids for the acylation. Results obtained in a study of the interaction of acetic acid and methyl lactate under various conditions show that acylation and acidolysis occur simultaneously, the principal products being methyl α -acetoxypropionate, α -acetoxypropionic acid, methyl acetate, and water. The combined yields of methyl α -acetoxypropionate and α -acetoxypropionic acid were high. Similar results were obtained when the study was extended to several alkyl lactates, glycolates, and α -hydroxyisobutyrate.

ALKYL lactates can be made in large quantities at low cost (21), and their acyl derivatives (alkyl α -acyloxypropionates, Equation 1) are of value as solvents, plasticizers (1, 2), and intermediates for the pyrolytic preparation of methyl acrylate (3, 19) and certain other polymerizable esters (7, 11, 20). Thus far, ketene (4), vinyl acetate (15, 16), acid anhydrides (6), and acid chlorides (8) have been used in the acylation of alkyl lactates,

Organic acids, although less expensive than their anhydrides and chlorides, have been considered less suitable for the acylation of alkyl lactates. It has been reported, for example, that methyl and ethyl acetate are formed when methyl and ethyl lactate, respectively, are treated with acetic acid (13).

The present authors have studied the reaction of alkyl lactates with acetic and propionic acids for the purpose of finding suitable conditions for making alkyl α -acyloxypropionates (reaction 1) and α -acyloxypropionic acids (reaction 2).



Most attention was directed to the interaction of methyl lactate, now commercially available, and acetic acid primarily because pyrolysis of the acetyl derivative of methyl lactate gives methyl acrylate, a resin and elastomer intermediate (17, 18), in high yield. As examples of other hydroxy esters, alkyl glycolates and α -hydroxyisobutyrate were included in the study. The present

TABLE I. EFFECT OF ENTRAINING AGENT ON REACTION OF METHYL LACTATE WITH ACETIC ACID^a

Entraining Agent	Reaction Conditions		Product, Mole		Total
	Time, hr.	Temp., ° C.	Methyl α-acetoxypropionate	α-Acetoxypropionic acid	
Benzene	5.0	91-93	0.35	0.51	0.86
Toluene	7.5	103-109	0.09	0.75	0.84
Cyclohexane	7.0	80-81	0.23	0.59	0.82
<i>n</i> -Hexane fraction ^b	11.0	69-71	0.17	0.75	0.92
Methylene chloride	14.5	63-65	0.19	0.52	0.71
Ethylene chloride	7.5	99-102	0.07	0.74	0.81
Isopropyl acetate	10.0	108-116	0.22	0.65	0.87

^a Reaction mixture: 1 mole methyl lactate, 6 moles acetic acid, 0.5 ml. sulfuric acid, approximately 200 ml. entrainer; this mixture was treated as described in the experimental section.

^b Mixture of hydrocarbons boiling at 63° to 70° C.

paper records the results obtained, and describes satisfactory methods for preparing α-acetoxypropionic acid, α-acetoxyisobutyric acid, and certain of their derivatives by the reaction of acetic acid with the corresponding hydroxy esters.

EXPERIMENTAL

The following example illustrates the general method: One mole of methyl lactate (104 grams), six moles of acetic acid (360 grams), 200 ml. of benzene, and 0.5 ml. of concentrated sulfuric acid were placed in a 1-liter round-bottom flask fitted with a thermometer through a side arm 10-mm. in inside diameter. The flask was attached to a 56-cm. Vigreux column that was well wrapped with asbestos insulation. The top of the column was fitted with a modified Barrett moisture trap (either plain or water-cooled), above which was placed a condenser. The reaction mixture was refluxed until 18 to 20 ml. of an aqueous layer collected in the trap, treated with sodium acetate to neutralize sulfuric acid, and then distilled through a Vigreux column. Benzene and excess acetic acid were removed under vacuum supplied by a water aspirator. The methyl α-acetoxypropionate and α-acetoxypropionic acid were distilled with an oil pump. The yields were 0.35 mole methyl α-acetoxypropionate and 0.51 mole α-acetoxypropionic acid.

This experiment, performed by J. H. Lengel, was repeated on a larger scale with toluene as an entraining agent. The material that distilled into the moisture trap contained the entraining agent, water, and methyl acetate, the latter being obtained in high yield. Hence, methyl acetate, α-acetoxypropionic acid, and methyl α-acetoxypropionate are the principal products of the reaction of methyl lactate with acetic acid under the conditions of the present study.

The principal by-products were distillation residues, which probably were derivatives of lactic acid and higher polymers of lactic acid (9). Presumably these distillation residues could be hydrolyzed to lactic acid or transformed into methyl lactate by treatment with methanol (10).

Commercially unavailable lactic esters needed for the acylation experiments were prepared as described in previous papers (7, 20).

Vigreux columns indented over a length of about 56 cm. were used in most instances to distill the reactants and the reaction products. One-liter flasks were used in most of the experiments.

When larger quantities were made in 5-liter flasks, with the same column and Barrett traps, higher and lower yields, respectively, of the α-acyloxy acid and α-acyloxy esters were obtained, and more time was required. Presumably the same reaction periods and yields would have resulted if proportionately larger apparatus had been used.

INTERACTION OF METHYL LACTATE AND ACETIC ACID

EFFECT OF ENTRAINING AGENT. Various entrainers were studied to determine their effect on the reaction of methyl lactate with acetic acid. High yields of α-acetoxypropionic acid were obtained with some of the entrainers, but the yields of methyl α-acetoxypropionate were low (Table I). Benzene was the best entrainer for producing methyl α-acetoxypropionate, whereas toluene, *n*-hexane fraction, and ethylene chloride were most suitable for making α-acetoxypropionic acid. The combined yield of acetyl derivatives was high except when methylene chloride was the entrainer. Possibly differences in boiling points and solubility characteristics of the entrainers were responsible for these varied effects.

In several experiments an ester corresponding to the acyl group of the organic acid and the alkoxy group of the alkyl lactate was used as the entrainer to determine whether the yield of the alkyl α-acyloxypropionate (reaction 1) would be increased by the following reaction: $R'COOCH(CH_3)COOH + R'COOR \rightarrow R'COOCH(CH_3)COOR + R'COOH$. The yield of the first product was not increased (Table II); this indicated that the conversion of the starting material does not occur readily under the conditions used. α-Acetoxypropionic acid reacts with methyl acetate at 100° to 150° C. (8) to yield methyl α-acetoxypropionate.

TABLE III. EFFECT OF SULFURIC ACID ON REACTION OF METHYL LACTATE WITH ACETIC ACID^a

H ₂ SO ₄ , Ml./Mole Methyl Lactate	Reaction Time, Hr.	Products, Mole		Total
		Methyl α-acetoxypropionate	α-Acetoxypropionic acid	
0	13	0.07 ^b	0	0.07
0.1	8	0.53	0.19	0.72
0.2 ^c	7	0.51	0.27	0.78
0.3	7	0.45	0.33	0.78
0.4	6	0.31	0.44	0.75
0.5	5	0.35	0.51	0.86
0.6	8	0.22	0.59	0.81
0.7	8	0.20	0.63	0.83
0.8	5	0.28	0.57	0.85
1.0	5	0.21	0.57	0.78

^a Reaction mixture: 1 mole methyl lactate, 6 moles acetic acid, 200 ml. benzene, concentrated sulfuric acid; reaction temperature: 89° to 95° C.

^b Most of the methyl lactate was recovered.

^c When this experiment was repeated on a fourfold scale, the yields of methyl α-acetoxypropionate and α-acetoxypropionic acid were 25 and 60%, respectively.

EFFECT OF SULFURIC ACID. As the amount of sulfuric acid per mole of methyl lactate was increased from 0.1 to 1 ml., the yield of methyl α-acetoxypropionate decreased from 53 to 21%, while the yield of α-acetoxypropionic acid increased from 19 to 57% (Table III). The total yield of acetylated products was 72% or higher in all instances. Acetylation occurred at a negligible rate in the absence of catalyst.

TABLE II. REACTION OF ALKYL LACTATES WITH ACIDS WHEN ESTER ENTRAINERS ARE USED

Entrainer, Moles	Alkyl Lactate, Moles	Acid, Moles	H ₂ SO ₄ , Ml.	Time, Hr.	Temp., ° C.	Aqueous Layer, Ml.	Products, Moles/Mole Alkyl Lactate		Total
							Alkyl α-acyloxypropionate	α-Acyloxypropionic acid	
<i>n</i> -Butyl acetate, 2	<i>n</i> -Butyl, 2	Acetic, 8	1	4	89-91	38	0.31	0.51	0.82
Methyl propionate, 4 ^a	Methyl, 2	Propionic, 8	0.6	11	100-104	36	0.32	0.40	0.72
	Methyl, 4	Propionic, 20	0.8	15	116-131	70	0.08	0.64	0.72
(Benzene, 200 ml.)	<i>n</i> -Butyl, 1	Acetic, 6	0.5	3.5	97-98	23	0.55	0.28	0.83
(Benzene, 200 ml.)	Methyl, 1	Propionic, 6	0.5	10	106-107	19	0.35	0.47	0.82

^a Methyl propionate, the entrainer, was formed in the early stages of the reaction.

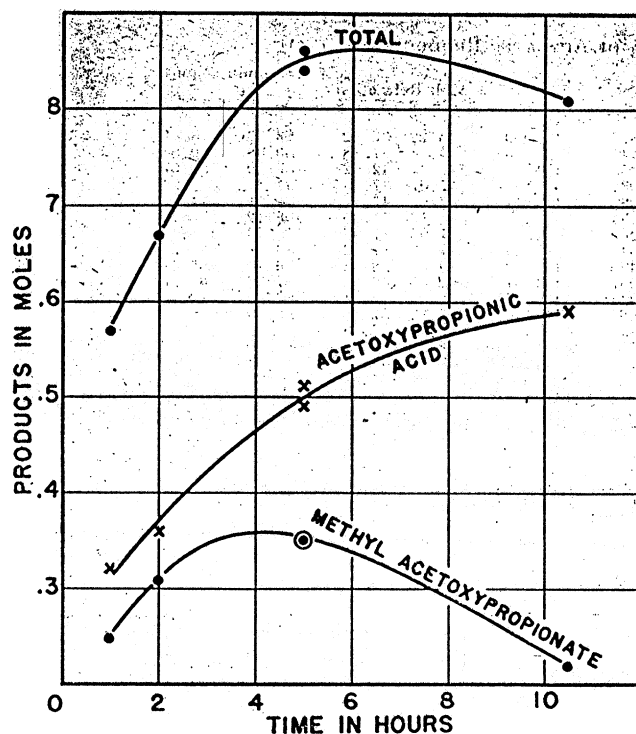


Figure 1. Acetylation of Methyl Lactate with Acetic Acid

Boric acid was not satisfactory as catalyst, although both methyl α -acetoxypropionate (22%) and α -acetoxypropionic acid (32%) were isolated; the yield of distillation residue was high. Little acetylation occurred when potassium acetate was used as catalyst, 80% of the methyl lactate being recovered. (The reaction mixture consisted of 1 mole methyl lactate, 6 moles acetic acid, 200 ml. benzene, and 5 grams potassium acetate.)

TABLE IV. EFFECT OF RATIO OF ACETIC ACID TO METHYL LACTATE*

Acetic Acid, Moles	Reaction Time, Hr.	Products, Mole		
		Methyl α -acetoxypropionate	α -Acetoxypropionic acid	Total
2	6.0	0.20	0.48	0.68
3	6.0	0.23	0.55	0.78
4	5.0	0.23	0.60	0.83
5	5.5	0.27	0.52	0.79
6	5.0	0.35	0.51	0.86
7	5.0	0.34	0.52	0.86
8	9.0	0.25	0.62	0.87
10	7.0	0.32	0.55	0.87

* Reaction mixture: 1 mole methyl lactate, 0.5 ml. sulfuric acid, acetic acid, benzene (100 ml. when 4 moles or less of acetic acid were used, 200 ml. for more than 4 moles).

EFFECT OF RATIO OF ACETIC ACID TO METHYL LACTATE. The yield of methyl α -acetoxypropionate increased from 20 to 35% as the molar ratio of acetic acid to methyl lactate was increased from 2 to 6 (Table IV). The total yield of acetylated products also increased as more acetic acid was used, whereas the yield of distillation residue decreased. The yield of distillation residue was high when only one mole of acetic acid per mole of methyl lactate was used.

EFFECT OF TIME. Reaction mixtures were refluxed for 1, 2, 5, and 10.5 hours (volume of aqueous layers in trap was 6, 8, 20, and 18 ml., respectively) to determine the effect of time. Conversion into methyl α -acetoxypropionate reached a maximum at about 4 hours, whereas conversion into α -acetoxypropionic acid increased with time up to 10 hours (Figure 1 and Table V). Presumably the smaller amount of water for the 10.5-hour period was caused

TABLE V. EFFECT OF TIME ON ACETYLATION OF METHYL LACTATE WITH ACETIC ACID*

H ₂ SO ₄ Catalyst, Ml.	Aqueous Layer, Ml.	Time, Hr.	Temp., ° C.		Products, Mole	
			Flask	Reflux	Methyl α -acetoxypropionate	α -Acetoxypropionic acid
0.5	6	1	92	72	0.25	0.32
0.5	8	2	92	69	0.31	0.36
0.5	20	5	91-93	69-71	0.35	0.51
0.5	20	5	92	67-70	0.35	0.49
0.6	18	10.5	90-95	64-76	0.22	0.59

* Reaction mixture: 1 mole methyl lactate, 6 moles acetic acid, 200 ml. benzene, sulfuric acid.

by evaporation of methyl acetate, a volatile component of the mixture.

ESTERIFICATION OF α -ACETOXYPROPIONIC ACID

It was shown previously (8) that α -acetoxypropionic acid can be converted satisfactorily into its methyl ester by passing the acid and methanol vapor countercurrently through a heated tower. The acetylation mixtures obtained in the present work are suitable for the same esterification procedure; thus it is possible to transform methyl lactate into methyl α -acetoxypropionate without acetic anhydride or ketene by the two steps: (a) reaction of methyl lactate with acetic acid, and (b) countercurrent treatment of the resulting mixture with methanol vapor.

The acetylation mixture used in the countercurrent esterification procedure (8) was prepared as already described from 4 moles methyl lactate, 24 moles acetic acid, 800 ml. benzene, and 0.8 ml. sulfuric acid. A portion of the resulting acetylation mixture was treated with sufficient sodium acetate to react with the sulfuric acid and then distilled. The distillation results showed that the yields of α -acetoxypropionic acid and methyl α -acetoxypropionate produced in the reaction were 60 and 25%, respectively.

Another portion of the acetylated mixture was heated (below 100° C.) under reduced pressure until most of the acetic acid had distilled. The residue, presumably a mixture of α -acetoxypropionic acid and methyl α -acetoxypropionate, was treated countercurrently with methanol vapor as previously described (8). (The authors are indebted to E. M. Filachione for these results.) Thus from a 2-mole aliquot treated for 3.5 hours at 86° to 102° C. at a pressure of 217 mm., there resulted a 20% conversion to methyl lactate and a 61% conversion to methyl α -acetoxypropionate (76% yield of methyl α -acetoxypropionate on the basis of material not converted into methyl lactate). A fraction having the boiling point of α -acetoxypropionic acid was collected also.

TABLE VI. REACTION OF HYDROXY ESTERS WITH ACETIC ACID*

Hydroxy Ester	Reaction Conditions		Product, Mole		
	Temp., ° C.	Time, hr.	Acetoxy ester	Acetoxy acid	Total
Methyl lactate	91-93	5.0	0.35	0.51	0.86
Ethyl lactate	93-95	5.5	0.38	0.50	0.88
Isopropyl lactate	96-97	4.0	0.66	0.17	0.83
n-Butyl lactate	97-98	3.5	0.55	0.28	0.83
Isobutyl lactate	96-99	4.5	0.45	0.35	0.80
Tetrahydrofurfuryl lactate	96-97	4.0	0.46
β -Butoxyethyl lactate	96-100	3.0	0.55
Methyl glycolate	89-91	4.5	0.31	0.50	0.81
Methyl glycolate ^b	104-110	5.0	..	0.73 ^c	..
Isobutyl glycolate	95-98	2.5	0.49	0.43	0.92
sec-Butyl glycolate	93-97	5.0	0.68	0.10 ^c	0.78
Methyl α -hydroxyisobutyrate	95-100	22.0	0.45	0.29 ^d	0.74
Methyl α -hydroxyisobutyrate ^b	110-114	23.0	..	0.68	..
Ethyl α -hydroxyisobutyrate	98-102	19.0	0.51
Ethyl α -hydroxyisobutyrate ^b	97-98	16.0	0.47	0.19 ^d	0.66

* Reaction mixture: 1 mole hydroxy ester, 6 moles acetic acid, 0.5 ml. sulfuric acid, 200 ml. benzene.

^b Reaction mixture: 1 mole hydroxy ester, 6 moles acetic acid, 1 ml. sulfuric acid, 150 ml. toluene.

^c This value is low owing to difficulty in distilling and collecting crystalline material.

^d α -Hydroxy isobutyric acid.

^e 0.8 ml. sulfuric acid used instead of 0.5 ml.

TABLE VII. PHYSICAL CONSTANTS OF ACYLATED PRODUCTS*

Compound	Boiling Point		d_4^{20}	n_D^{20}	Mol. Refraction		Saponification Equiv.	
	° C.	Mm.			Calcd.	Found	Calcd.	Found
Methyl α -acetoxypropionate	172	Atm.	1.0875	1.4090	33.22	33.22	73.07	73.53
Ethyl α -acetoxypropionate	181	Atm.	1.0441	1.4085	37.84	37.88	80.08	80.81
Isopropyl α -acetoxypropionate	76	13.3	1.0053	1.4068	42.45	42.62	87.10	87.57
<i>n</i> -Butyl α -acetoxypropionate	90	7.8	1.0036	1.4163	47.07	47.09	94.11	95.20
Isobutyl α -acetoxypropionate	74	5.3	0.9982	1.4140	47.07	47.11	94.11	94.43
Tetrahydrofurfuryl α -acetoxypropionate	109	1.2	1.1234	1.4445	51.13	51.18	108.12	108.17
β -Butoxyethyl α -acetoxypropionate	116	3.2	1.0262	1.4255	57.95	57.93	116.13	115.41
Methyl α -propionoxypropionate	65	6.8	1.0540	1.4120	37.83	37.82	80.08	80.07
Methyl acetoxyacetate	173	Atm.	1.1426	1.4100	28.60	28.64	66.1	65.4
Isobutyl acetoxyacetate	61-2	2	1.0267	1.4161	42.45	42.58	87.10	88.20
<i>sec</i> -Butyl acetoxyacetate	51	0.4	1.0243	1.4143	42.45	42.51	87.10	87.76
Methyl α -acetoxyisobutyrate	59	8.9	1.0586	1.4140	37.83	37.82	80.09	80.19
Ethyl α -acetoxyisobutyrate	74	14.6	1.0215	1.4125	42.45	42.48	87.09	87.11
α -Acetoxypropionic acid	101	1.8	1.1758 ^b	1.4240 ^b	28.60	28.67	66.06	66.03
α -Propionoxypropionic acid	108	2.2	1.1262 ^b	1.4250 ^b	33.22	33.18	73.07 ^c	73.04 ^c
Acetoxyacetic acid ^d	113-4	4.6
α -Acetoxyisobutyric acid ^e	92	0.8	...	1.4265 ^b

* Water solubilities (grams per 100 grams water at room temperature) for the methyl, ethyl, isopropyl, *n*-butyl, and isobutyl esters of α -acetoxypropionic acid were 8, 3.2, 1.4, 0.3, and 0.3, respectively; water solubility of methyl α -propionoxypropionate was 2.2. These were determined by a modification (ester containing Sudan red added from weighed bottle to 50 ml. water in an iodine flask) of the method of Fordyce and Meyer (12). Methyl α -propionoxypropionate: calcd., C, 52.5; H, 7.6; found, C, 52.6; H, 7.6. α -Propionoxypropionic acid: calcd., C, 49.3; H, 6.9; found, C, 49.8; H, 7.1. Methyl α -acetoxyisobutyrate was prepared also by the continuous acetylation of methyl α -hydroxyisobutyrate, with previously described method and equipment (6).

^b Determined with supercooled material.

^c Equivalent weight based on total alkali used.

^d M. p. 64-66° C. (crystallized from benzene); Anschütz and Bertram (1) reported 66-68° C.

^e M. p. 59-60° C. (solidified distillate); Anschütz and Motschmann (2) reported 61° C.

MISCELLANEOUS HYDROXY ESTERS

Various lactic esters, alkyl glycolates, and alkyl α -hydroxyisobutyrate were generally similar in behavior to methyl lactate when treated with acetic acid (Table VI). In harmony with the fact that alkyl glycolates and α -hydroxyisobutyrate are primary and tertiary alcohols, respectively, the glycolates reacted more rapidly than alkyl lactates, whereas the α -hydroxyisobutyrate reacted less rapidly (as judged by accumulation of aqueous layer in moisture trap). The acylation of benzyl α -hydroxyisobutyrate with capric acid has been reported by Thurston and Grim (22). Distillation of the reaction products revealed a difference between α -hydroxyisobutyrate on one hand and glycolates and lactates on the other. The fraction that distilled immediately after methyl or ethyl α -acetoxyisobutyrate was α -hydroxyisobutyric acid; this showed that α -hydroxyisobutyric acid as well as α -acetoxyisobutyric acid was produced in the reaction. Although glycolic and lactic acids were not obtained as distillates in the alkyl glycolate and alkyl lactate experiments, it is possible that they were formed and transformed into polymeric materials (recovered as residues) before or during distillation.

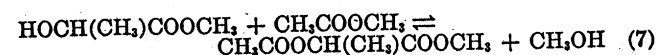
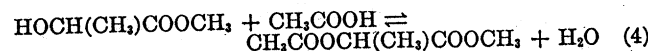
In some instances the α -acetoxy esters (Table VII) were obtained in relatively high yields (Tables VI and VII); this showed that it is feasible to use acetic acid as the acetylating agent in preparing compounds such as isopropyl, butyl, and β -butoxyethyl α -acetoxypropionate, butyl acetoxyacetate, and ethyl α -acetoxyisobutyrate. The highest yields of acetoxy ester were obtained from esters of secondary alcohols—that is, isopropyl lactate and *sec*-butyl glycolate.

The yield of acetoxy ester was lowest when methyl lactate or methyl glycolate was allowed to react with acetic acid. This suggests that the low yields of methyl α -acetoxypropionate and methyl acetoxyacetate were largely due to the rapid formation and volatilization of methyl acetate.

DISCUSSION

The reactions (some of which are shown below) and equilibria that may result when methyl lactate and acetic acid are heated in the presence of sulfuric acid are numerous, and the specific reactions responsible for the products are not known. In addition to the products (water, methyl acetate, methyl α -acetoxypropionate, α -acetoxypropionic acid, acetyl derivative of lactic acid, and distillation residue) actually isolated, the following also

might be formed: lactic acid, lactylactic acid, lactide, methyl lactylactate, and methanol.



It was observed that methyl acetate and water are formed rapidly during the interaction of methyl lactate and acetic acid, and hence reaction 3 probably is responsible for the formation of methyl acetate. Reactions 4 and 5 could be responsible for the formation of water. Since methyl acetate (boiling point 57° C.) is readily volatilized, apparently it is present only in low concentrations and can function as a reactant (reaction 7 and the reverse of reactions 3 and 6) only to a limited extent. Probably reaction 4 is more responsible for the formation of methyl α -acetoxypropionate than are reactions 7 and 8 and the reverse of reaction 6. Methyl α -acetoxypropionate reacted slowly with acetic acid, and therefore it seems likely that little of the α -acetoxypropionic acid was formed by reaction 6; reaction 5 appears to be a more reasonable source of α -acetoxypropionic acid. Methyl α -acetoxyisobutyrate was almost completely unreactive in the presence of boiling acetic acid and a small quantity of sulfuric acid.

Grummitt and Fleming (14) studied the acetylation of castor oil (glyceryl ricinoleate) and observed that acetylation but not acidolysis occurred when water was removed continuously during the reaction. Both acidolysis and acetylation occurred when methyl lactate was treated with acetic acid even under essentially anhydrous conditions and with the continuous removal of water.

Cohen (5) stated that esters of secondary alcohols undergo acidolysis more readily than those of primary alcohols. This effect does not appear to predominate for alkyl lactates under the conditions studied (Table V).

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